Soil Exchangeable Phosphorus Pools, Equilibrium Characteristics, and Mass Distribution Coefficients for Eight-Mile Run Watershed, Wisconsin

by William F. James, Billy E. Johnson, Zhonglong Zhang, Charles W. Downer, and Aaron R. Byrd

PURPOSE: This research experimentally determined phosphorus mass distribution coefficients (i.e., relationship between soil exchangeable and soluble phosphorus), exchangeable phosphorus pools, and soluble phosphorus in the interstitial water for soils exhibiting a range of phosphorus concentrations. The research also developed relationships between these variables and commonly measured, crop-available soil phosphorus for use in establishing initial soil P parameters in the System-Wide Water Resources Program-Nutrient Sub-Model (SWWRP-NSM).

BACKGROUND: Mass transfer of soluble phosphorus (P) between soil and laminar overland flow can be described as:

$$S_d = k_e \left(\frac{C_{d2}}{\varphi - C_d} \right) \tag{1}$$

where

S_d = the mass transfer flux ($M \cdot L^{-2} \cdot T^{1}$)
C_d = the concentration of soluble P in the water column ($M \cdot L^{-3}$)
C_{d2} = the concentration of soluble P in the soil interstitial water ($M \cdot L^{-3}$; also referred to as the equilibrium P concentration or EPC, Froelich 1988)
k_e = the mass transfer coefficient ($L \cdot T^{-1}$)
φ = the porosity (dimensionless; Wallach et al. 1988; Chapra 1997; Gao et al. 2004).

C_{d2} can rapidly (i.e., hours) exchange with P that is reversibly adsorbed to soil constituents (primarily on Al and Fe hydroxides) until an approximate equilibrium is achieved between particulate and aqueous phases as:

$$C_{d2} \rightleftharpoons C_{p2} \tag{2}$$

where C_{p2} = the soil adsorbed inorganic P pool ($M \cdot M^{1}$; Barrow 1983; Van Riemsdijk et al. 1984). In general, C_{p2} represents a small fraction of the total adsorbed inorganic P pool and a smaller fraction of the total potential capacity for soils to adsorb P. Shifts in P equilibrium due to crop uptake or fertilizer application can result in rapid (on the order of minutes to hours) exchanges between the particulate and aqueous phases. For example, P desorption from soil

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occurs when C_{d2} declines below equilibrium conditions and P adsorption to soil occurs when C_{d2} exceeds equilibrium conditions.

The total concentration of this exchangeable inorganic P pool (C_{T2}; $M \cdot L^{-3}$) in the surface soil layer can be divided into two components as:

$$C_{T2} = (1-\varphi) \cdot \rho \cdot C_{p2} + \varphi C_{d2} \tag{3}$$

where ρ = the soil density ($M \cdot L^{-3}$). C_{d2} and C_{p2} are related to an equilibrium partition coefficient as:

$$C_{p2} = k_{d2} \cdot C_{d2} \tag{4}$$

where k_{d2} = the mass distribution coefficient ($L^3 \cdot M^{-1}$). Equations 3 and 4 can be combined as:

$$C_{T2} = C_{d2} \cdot (\alpha + \varphi) \tag{5}$$

where

$$\alpha = (1-\varphi) \cdot \rho \cdot k_{d2} \tag{6}$$

Alternatively, Equation 4 can be solved for C_{d2} and combined with Equation 3 as:

$$C_{T2} = C_{p2} \cdot (\alpha + \varphi) \cdot k_{d2}^{-1} \tag{7}$$

In order to model soluble P transfer between soil and overland flow, C_{T2}, C_{p2}, C_{d2}, and k_{d2} need to be initialized in SWWRP-NSM. This information is not readily available and usually must be determined experimentally via Langmuir isotherm assays. Numerous studies have shown that P mass transfer varies positively as a function of the concentration of various adsorbed P pools and the degree of soil P saturation (Pote et al. 1996; McDowell et al. 2001; Torbert et al. 2002; Vadas et al. 2005), indicating relationships between P mass transfer and soil management practices. In addition, extraction techniques have been used to approximate ranges in C_{d2} and C_{p2} (see review by McGrechan 2002). Finally, Fang et al. (2002) demonstrated relationships between the EPC and adsorbed P pools. Little is known about variations in k_{d2} as a function of adsorbed soil P (Lewis and McGrechan 2002). However, this information is critical for soil mass transfer modeling, since C_{T2}, C_{p2}, C_{d2}, and k_{d2} are inter-related (i.e., Equations 5 and 7). In particular, k_{d2} may not be constant, but rather declines with increasing soil P concentration due to decreasing availability of unoccupied adsorption sites. The objectives of this research were to 1) estimate C_{T2}, C_{p2}, C_{d2}, and k_{d2} for soils with widely ranging P concentrations, and 2) develop empirical relationships between these variables and commonly measured Bray and Mehlich P (i.e., extractable crop-available P) for use in establishing initial soil P parameters for SWWRP-NSM (Johnson et al. 2008).

METHODS:

Study Site. Eight-Mile Run is a 264-ha sub-watershed located in the Upper Eau Galle River Basin, west-central Wisconsin (Figure 1). Livestock (dairy) pasture and associated barnyards represent approximately 6 percent of the watershed. This land use is located immediately adjacent to the tributary in the lower portion of the watershed. Alfalfa and corn production represent approximately 49 percent, and grass, CRP, and wooded land uses occupy approximately 45 percent of the watershed. Crop production occurs in the northern, eastern, and southeastern regions of the watershed. Grass, CRP, and wooded areas are located in the north-central and western portions of the watershed. The watershed is bisected into approximately equal areas by a railroad and U.S. Route 12. Grass, CRP, and wooded areas account for 61 percent while livestock and crop production represent 69 percent of the land use in the upper and lower portions of the watershed, respectively.
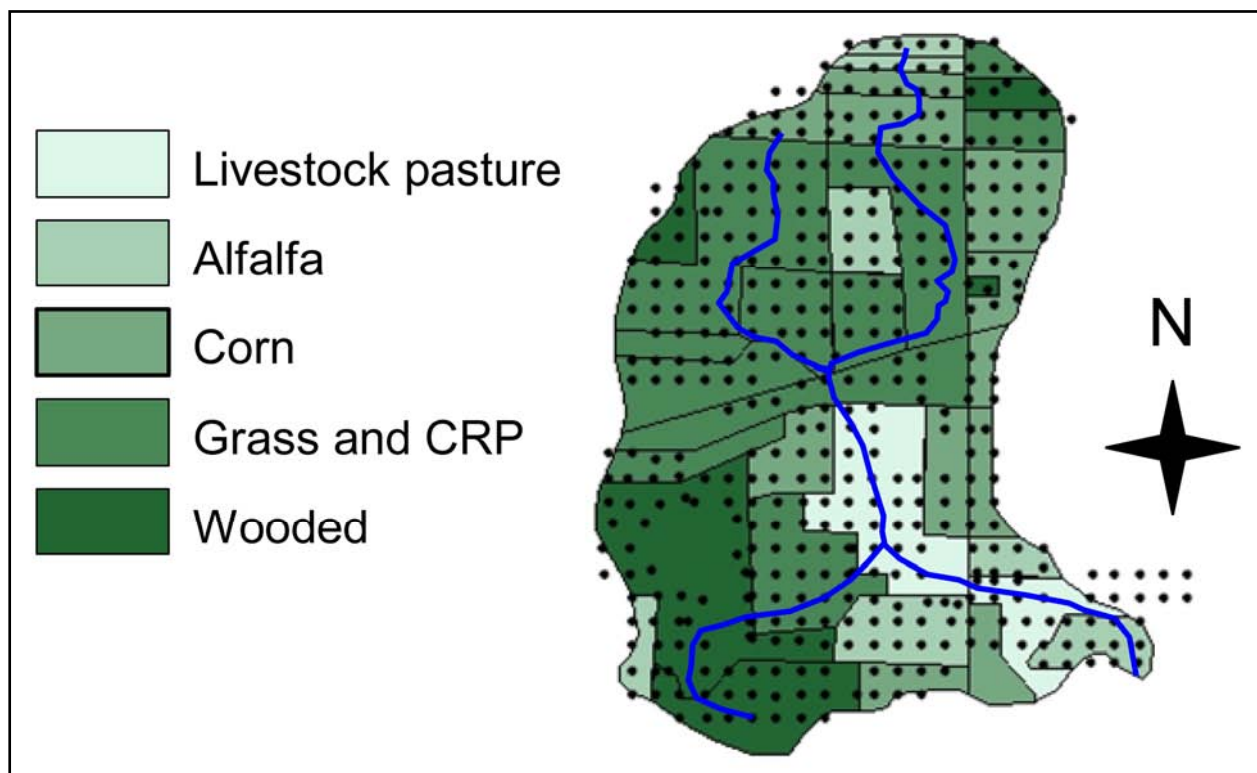

Figure 1.   A map of the Eight-Mile Run watershed showing various land uses. Solid circles represent soil sampling locations.

Field Soil Collection Procedures. A 75-m sampling grid was established in the Eight-Mile Run watershed for soil sampling between June and early July, 2006 (Figure 1). Stations were located using high resolution digital orthophotographs and differential GPS (Garmin model 72; Garmin International, Olathe, KS, USA). Vegetation was clipped to ground level at each sampling point and six 5-cm-deep soil cores were collected around a 2-m-diam circle. The soil cores collected at each station were combined into one composited sample. Land use was recorded at the time of sampling. In the laboratory, soils were passed through a 2-mm mesh screen to remove root material and air dried at 25 °C. Overall, approximately 430 composited

soil samples were collected from the Eight-Mile Run watershed. The dried soil samples were further composited for chemical analyses as a function of 37 fields exhibiting homogeneous land uses (Figure 1).

Soil Phosphorus Pools and Equilibrium Characteristics. Soil was extracted in 0.025 M HCl and 0.03 M NH_4F and a solution containing 0.2 M CH_3COOH, 0.25 M NH_4NO_3, 0.015 M NH_4F, 0.013 M HNO_3, and 0.001 M EDTA for determination of crop-available Bray and Mehlich-3 P, respectively (Pierzynski 2000). Langmuir isotherm assays were conducted according to methods described in Nair et al. (1984). Soils were subjected to initial P (as KH_2PO_4-P in a 0.01 M $CaCl_2$ solution) concentrations of 0, 0.125, 0.25, 0.50, 1, 5, 10, 25, 50 and 100 $mg·L^{-1}$ using a soil:solution ratio of 1:25 (40 $g·L^{-1}$). The soil solution tubes were gently shaken in a darkened environment at 20 °C over a 24-hr period. The equilibrated samples were centrifuged at 500 g and filtered through a 0.45-μ filter for soluble reactive P (SRP) determination (American Public Health Association (APHA) 1998).

The change in SRP mass [(initial C_{d2} - final C_{d2})·solution volume] was divided by soil mass to determine the mass of P desorbed or adsorbed from soil (ΔC_{p2}; $mg·kg^{-1}$). ΔC_{p2} was plotted as a function of final C_{d2} (i.e., equivalent to C_{d2} in Equation 1) to determine the mass distribution coefficient (k_{d2}; $L·kg^{-1}$), the equilibrium phosphorus concentration (EPC, the point where net sorption is zero and equivalent to C_{d2}; Froelich 1988), and the concentration of the initial adsorbed P pool (C_p; $mg·kg^{-1}$). k_{d2}, C_{d2}, and C_{p2} (i.e., equivalent to C_{p2} in Equation 1) were calculated via regression analysis (Statistical Analysis System 1994) from linear relationships between final C_{d2} and ΔC_{p2} near the point where net sorption was zero (i.e., crossover point; Figure 2). k_{d2} was equal to the slope of the regression line and C_{p2} was estimated as the intercept. This calculation was modified for soils with very high P content because the ΔC_{p2} versus C_{d2} relationship was nonlinear near the crossover region and linear regression of these data would have resulted in an underestimate of C_{p2} (Figure 3). Under these conditions, C_{p2} was estimated via regression analysis at very low C_{d2} and k_{d2} was calculated as the slope of the line between C_{p2} and positive ΔC_{p2} (i.e., net adsorption of P) nearest the crossover point.

The P sorption capacity (PSC; $M·L^{-3}$) was estimated as ΔC_{p2} for soils subjected to a 100 $mg·L^{-1}$ solution (Nair et al. 1998). The degree of P saturation index (DPS_{Index}; %) was calculated as:

$$DPS_{Index} = 100 \bullet \left[\frac{P_{Adsorbed}}{PSC + P_{Adsorbed}} \right]$$

(8)

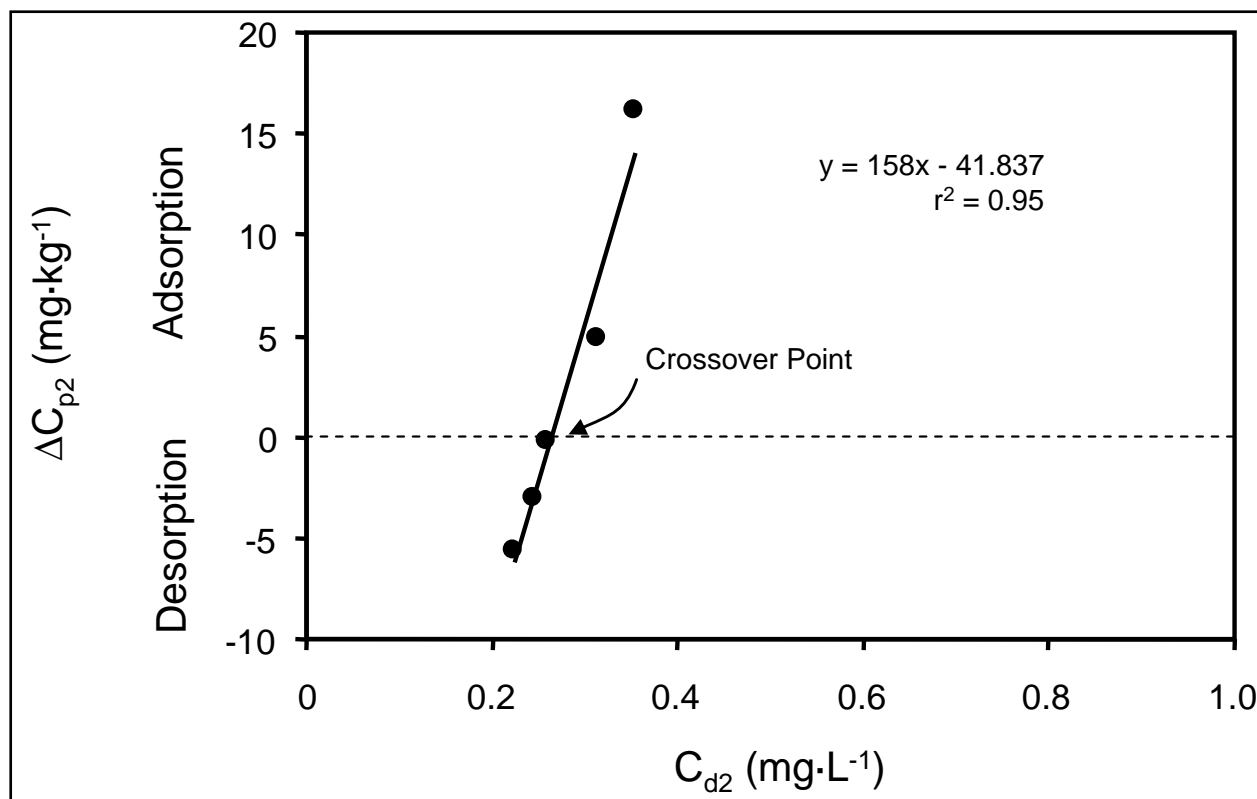where $P_{Adsorbed}$ was either Bray or Mehlich P.

Figure 2. An example of an adsorption-desorption isotherm. C_{d2} represents the concentration of soluble reactive phosphorus in the aqueous phase after continuous shaking with soil over a 24-hr period. ΔC_{p2} represents the change in soluble reactive phosphorus concentration after the 24-hr shaking period (initial C_{d2} - final C_{d2}) normalized with respect to soil mass. A negative ΔC_{p2} indicates desorption of phosphorus from soil to the aqueous phase while a positive ΔC_{p2} represents adsorption of aqueous phosphorus onto soil particles. The crossover point is equivalent to the equilibrium phosphorus concentration (EPC). The slope of the regression equation near the crossover point is the mass distribution coefficient (k_{d2}; $L \cdot kg^{-1}$). The intercept of the regression equation represents initial adsorbed soil phosphorus concentration (C_{p2}; $mg \cdot kg^{-1}$).
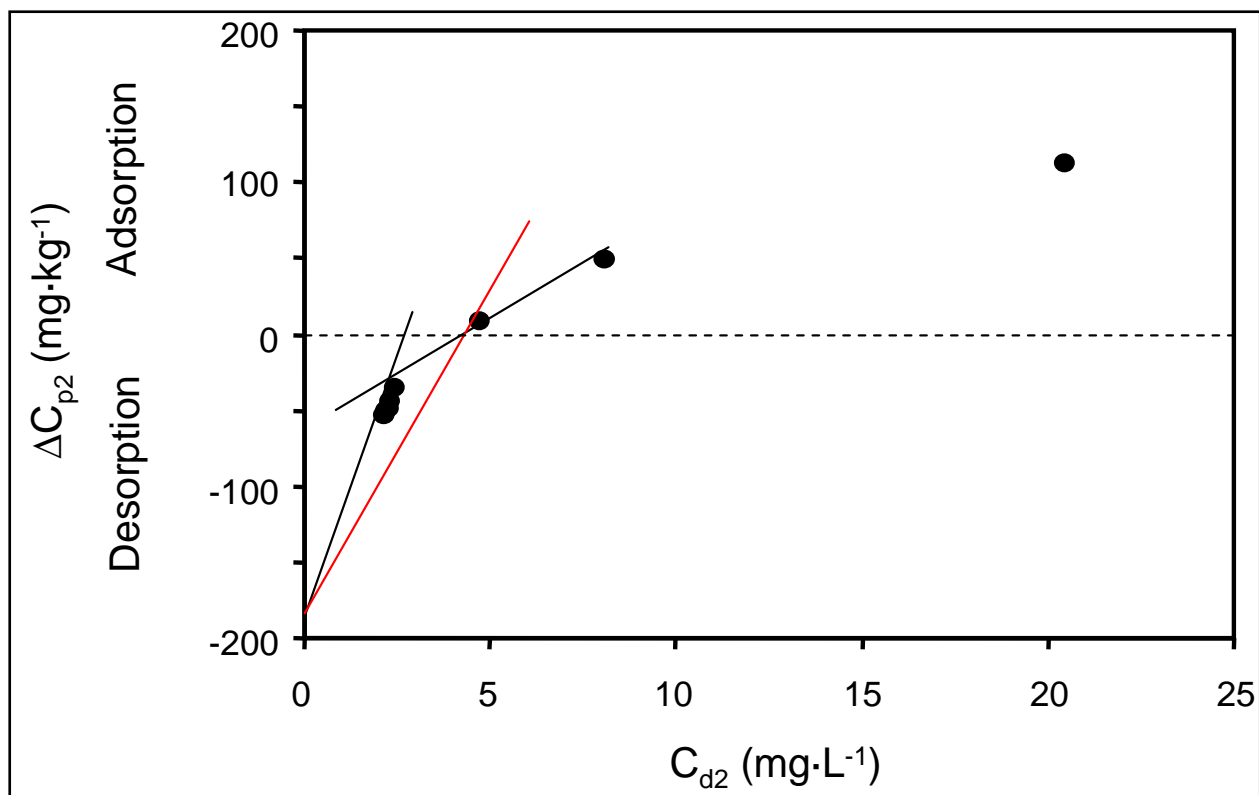
Figure 3. Adjustment used to determine k_{d2}, C_{d2}, and C_{p2} for soils with very high soil Bray and Mehlich-3 P concentrations and nonlinear patterns near the crossover point. C_{p2} is estimated as the intercept for the linear portion of the isotherm at low C_{d2} concentrations. k_{d2} is calculated as the slope of a line passing through C_{p2} and the first data point above the crossover (i.e., positive ΔC_{p2}). The red line represents the adjusted k_{d2} slope.

RESULTS AND DISCUSSION: Bray and Mehlich P exceeded 30 mg·kg^{-1} and 50 mg·kg^{-1} (optimum for crop growth), respectively, primarily in the lower portion of the watershed in conjunction with crop and livestock production land use practices (Figure 4). CRP, grasses, and woodlot land uses were associated with Bray and Mehlich P concentrations that were at or below optimum levels for crop uptake.

Examples of ΔC_{p2} versus C_{d2} are shown for four fields in Figure 5. High k_{d2} was associated with low C_{d2}, crop-available P, and C_{p2}. It declined in conjunction with higher soil P concentrations. For all fields, k_{d2} covaried nonlinearly as a function of crop-available P (Figures 6a and 6b). It was greatest for soils with low Bray and Mehlich P and declined in a negative logarithmic pattern with increasing soil P. These patterns may be related to differences in the degree of P saturation of sorption sites (Kleinman et al. 2000). For instance, the soil buffering capacity to adsorb P under conditions of P disequilibrium would decline as DPS increases due to a lower number of unoccupied adsorption sites, resulting in lower P sorption efficiency (see below and Figure 7).
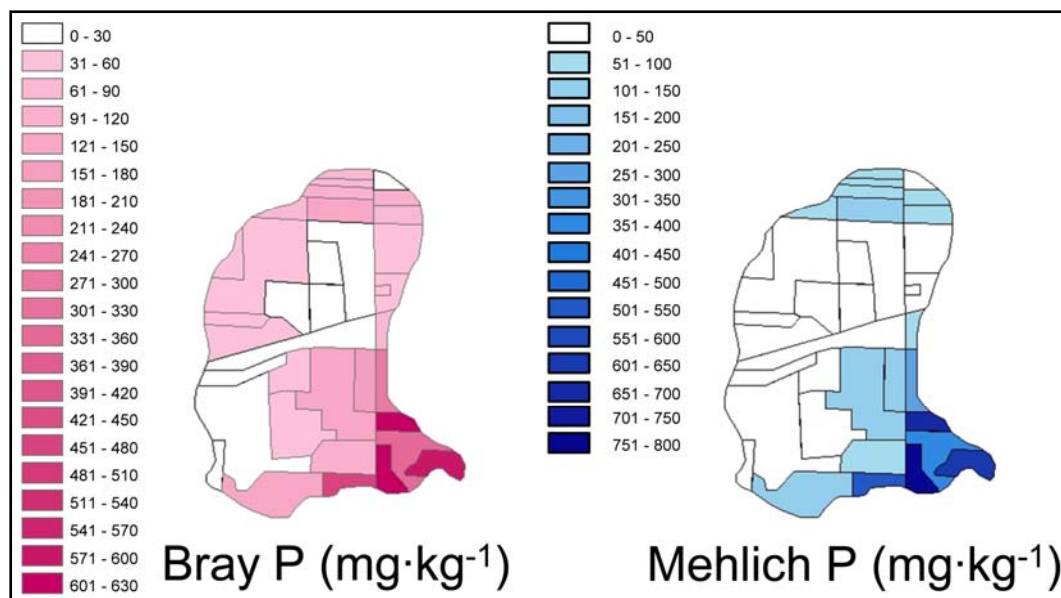
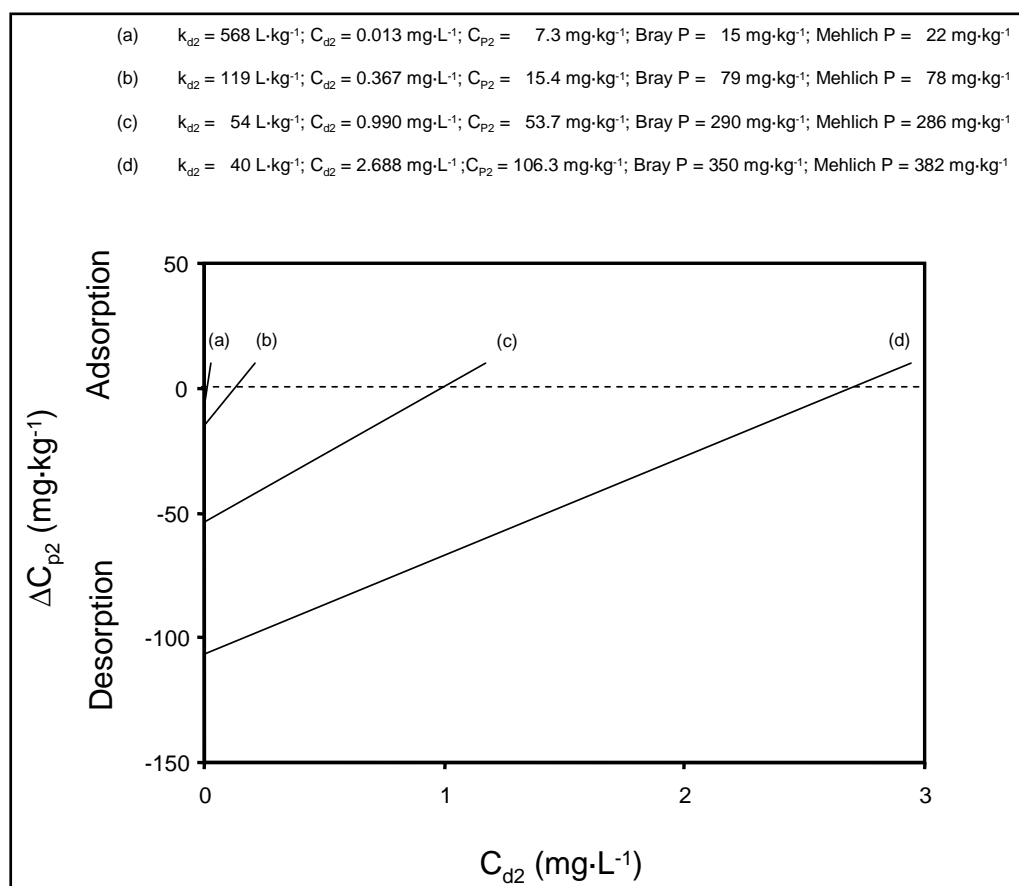Figure 4. Spatial variations in soil Bray and Mehlich-3 P concentrations in Eight-Mile Run in 2006.

(a) k_{d2} = 568 L·kg^{-1}; C_{d2} = 0.013 mg·L^{-1}; C_{P2} = 7.3 mg·kg^{-1}; Bray P = 15 mg·kg^{-1}; Mehlich P = 22 mg·kg^{-1}

(b) k_{d2} = 119 L·kg^{-1}; C_{d2} = 0.367 mg·L^{-1}; C_{P2} = 15.4 mg·kg^{-1}; Bray P = 79 mg·kg^{-1}; Mehlich P = 78 mg·kg^{-1}

(c) k_{d2} = 54 L·kg^{-1}; C_{d2} = 0.990 mg·L^{-1}; C_{P2} = 53.7 mg·kg^{-1}; Bray P = 290 mg·kg^{-1}; Mehlich P = 286 mg·kg^{-1}

(d) k_{d2} = 40 L·kg^{-1}; C_{d2} = 2.688 mg·L^{-1}; C_{P2} = 106.3 mg·kg^{-1}; Bray P = 350 mg·kg^{-1}; Mehlich P = 382 mg·kg^{-1}

Figure 5. Variations in the soil mass distribution coefficient (k_{d2}), equilibrium soluble phosphorus concentration (C_{d2}), and soil adsorbed phosphorus concentration (C_{p2}) for four soils exhibiting different Bray and Mehlich-3 phosphorus concentrations.
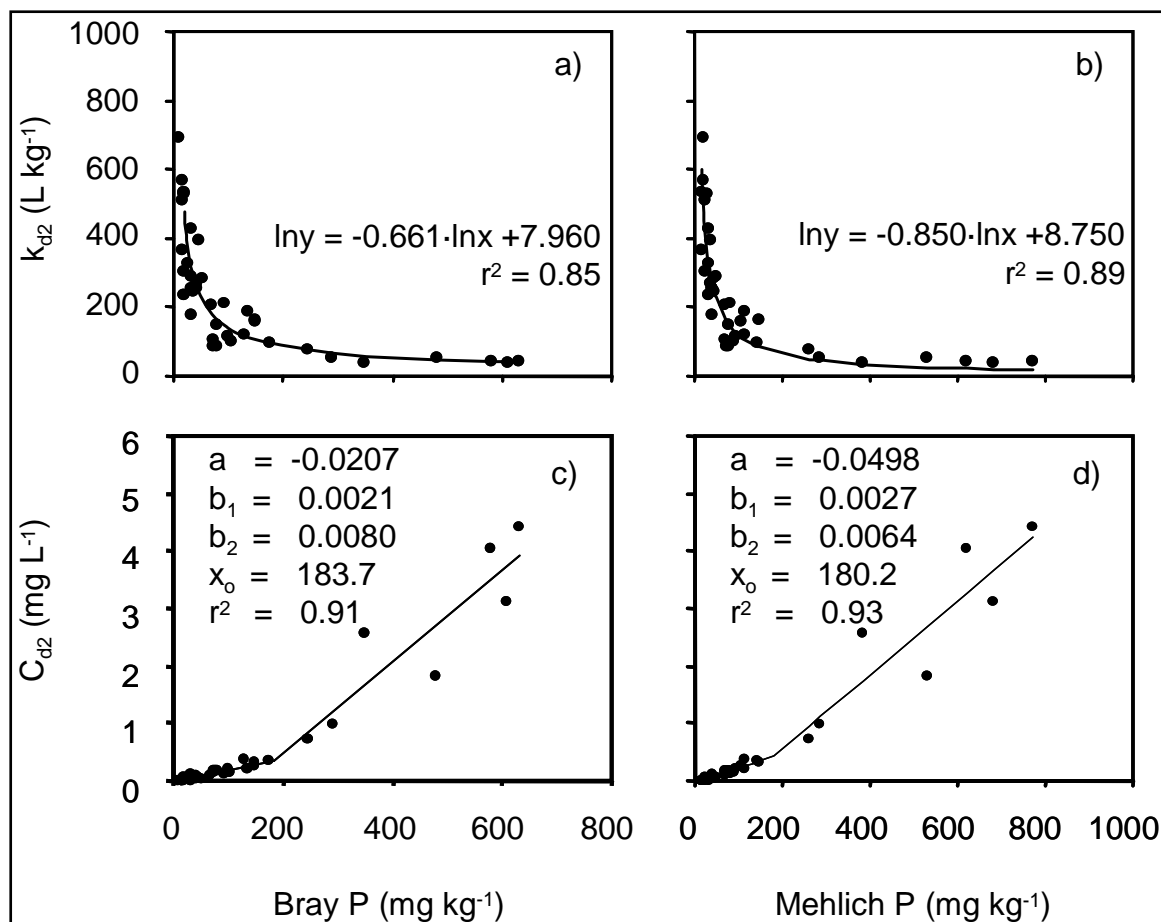
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Figure 6. The soil mass distribution coefficient (k_{d2}; panels a and b) and the equilibrium soluble phosphorus concentration (C_{d2}; panels c and d) versus soil Bray and Mehlich-3 phosphorus. The NLIN procedure (Statistical Analysis System 1994) was used to estimate the coefficients a, b_1, b_2, and X_o. See Equations 7 and 8 for a description.
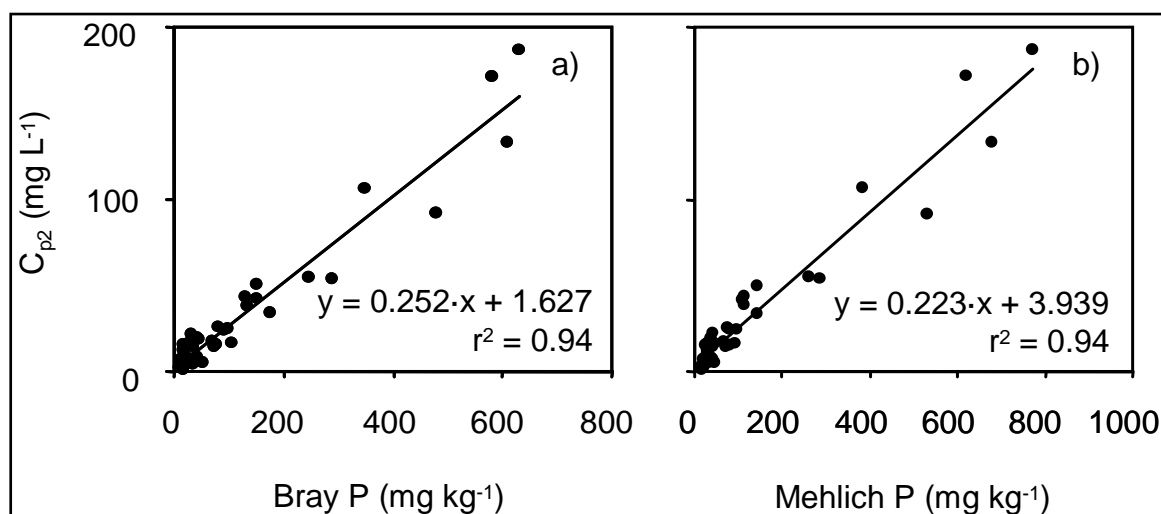

Figure 7. Initial adsorbed soil phosphorus (C_{p2}) versus soil Bray and Mehlich-3 phosphorus.

C_{d2} exhibited a biphasic linear increase as a function of crop-available P (Figures 6c and 6d). These patterns could be interpreted using a segmented linear-linear regression analysis (NLIN; Statistical Analysis System 1994) that estimates a threshold between regression lines (Kleinman et al. 2000). Linear models are:

$$y = a + (b_1 \cdot x) \tag{9}$$

$$y = a + (b_1 \cdot x_o) + b_2 \cdot (x - x_o) \tag{10}$$

where a, b_1, and b_2 are constants and x_o is the Bray or Mehlich P threshold concentration. x_o was similar for Bray and Mehlich P at 183.7 and 180.2 mg·kg^{-1}, respectively. At these threshold levels, C_{d2} was ~0.4 mg·L^{-1} for Bray and Mehlich P, respectively. Above these levels, the rate of change in C_{d2} with respect to Bray or Mehlich P increased (Figures 6c and 6d). Similar to k_{d2}, these patterns are likely related to increasing DPS. As sorption sites become increasingly saturated, buffering capacity declines, resulting in greater equilibrium C_{d2}. Strong linear relationships were observed between Bray or Mehlich P and C_{p2} (Figure 7). Overall, C_{p2} represented approximately 25 percent of the Bray and Mehlich P concentration.

Land uses associated with crop and livestock production in the lower portion of the watershed exhibited the highest DPS$_{Bray}$ and DPS$_{Mehlich}$ (Figure 8). Both indices approached 80-percent saturation in conjunction with high Bray and Mehlich P (Figure 4). k_{d2}, C_{d2}, and C_{p2} covaried similarly with increasing DPS$_{Bray}$ and DPS$_{Mehlich}$ (Figure 9). k_{d2} declined logarithmically while C_{d2} increased in a linear biphasic pattern with increasing DPS$_{Bray}$ and DPS$_{Mehlich}$. Threshold values for DPS$_{Bray}$ and DPS$_{Mehlich}$ were 37.3 percent and 39.1 percent, respectively, coinciding with a C_{d2} of ~ 0.4 mg·L^{-1}. Regression relationships between C_{p2} and DPS$_{Bray}$ or DPS$_{Mehlich}$ were linear and positive (Figure 9).
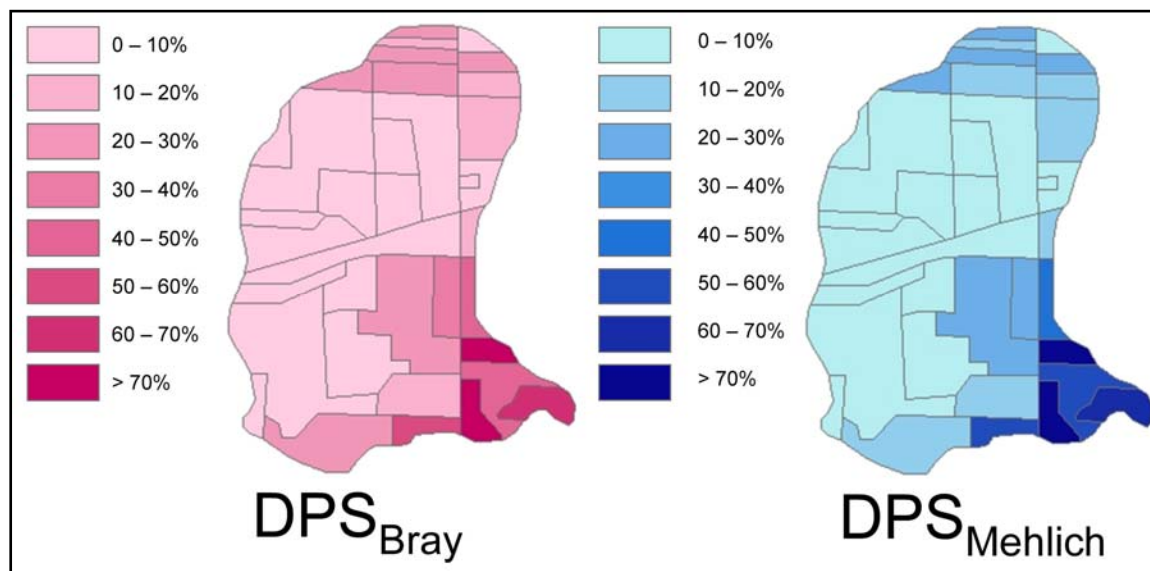

Figure 8. Spatial variations in the degree of phosphorus saturation (DSP), based on soil Bray and Mehlich-3 phosphorus concentration.
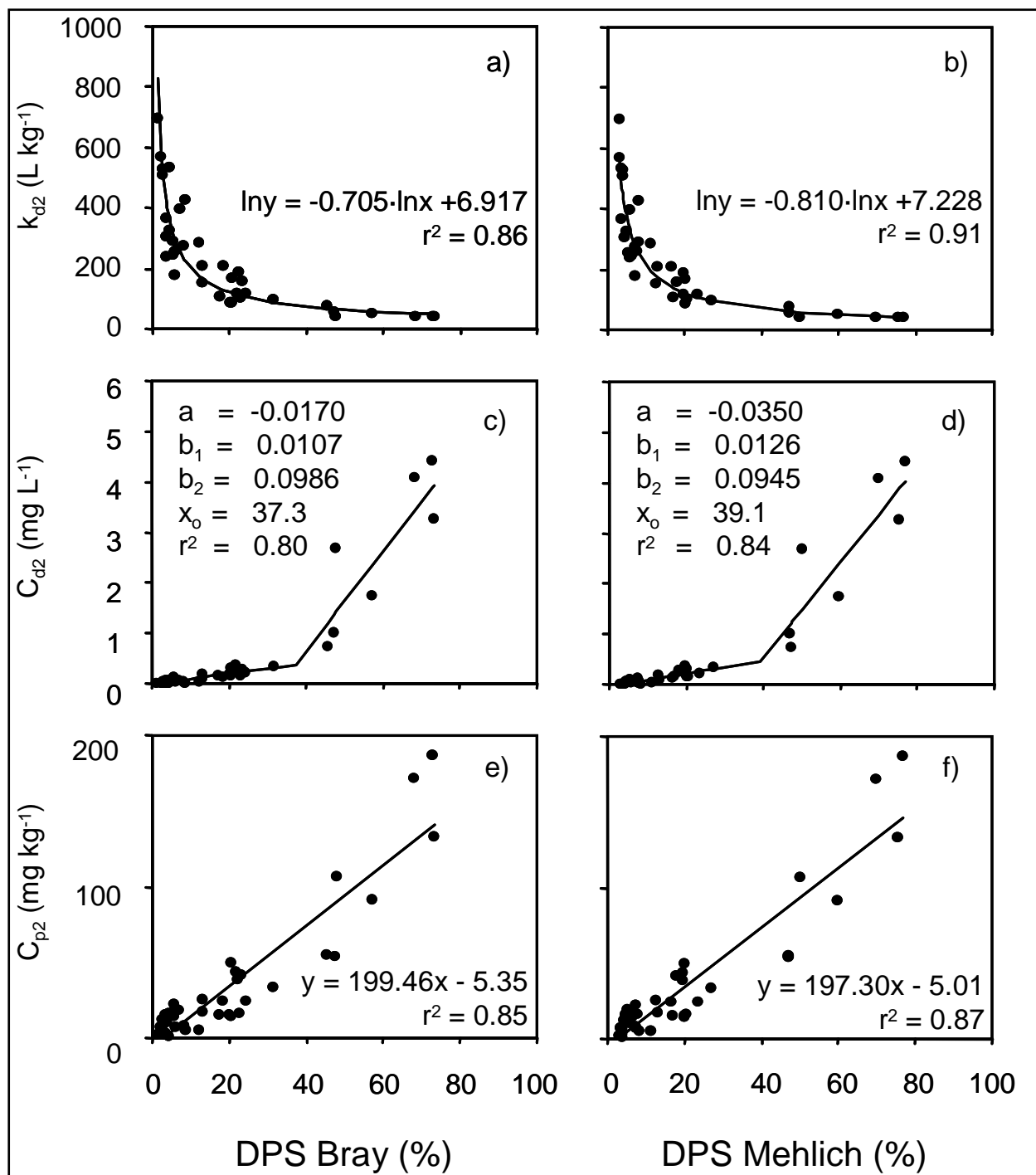
Figure 9. The soil mass distribution coefficient (kd2; panels a and b), equilibrium phosphorus concentration (Cd2; panels c and d), and the initial adsorbed soil phosphorus concentration (Cp2; panels e and f) versus the degree of phosphorus saturation (DPS) based on soil Bray and Mehlich-3 phosphorus concentration.

An important finding of this study is that commonly measured crop-available P can be used to initialize C_{p2}, C_{d2}, and k_{d2} in SWWRP-NSM. Empirical regression equations are summarized in Table 1. Relationships between observed and predicted variables were highly significant and slopes were near 1.0 (Figure 10). C_{T2} can be estimated from Equation 3. Additional information on C_{p2}, C_{d2}, and k_{d2} is needed for a variety of soil types in order to develop general empirical patterns for initializing these variables in SWWRP-NSM.

Table 1
Empirical Equations for Initializing k_{d2}, C_{d2}, and C_{p2} in SWWRP-NSM Using Commonly Measured Soil Bray or Mehlich-3 Phosphorus (P).
x = Bray or Mehlich P (mg/g)

Dependent variable, y	Bray P regression equations	Mehlich P regression equations
k_{d2}, L·kg^{-1}	ln(y) = -0.661·ln(x) + 7.960 For x ≤ 183.7 mg·kg^{-1} Bray P - 0.02067 + 0.00208·x	ln(y) = -0.850·ln(x) + 8.750 For x ≤ 180.2 mg·kg^{-1} Mehlich P - 0.04982 + 0.00267·x
C_{d2}, mg·L^{-1}	For x > 183.7 mg·kg^{-1} Bray P 0.36118 + 0.0080·(x - 183.7)	For x > 180.2 mg·kg^{-1} Mehlich P 0.4297 + 0.0064·(x - 180.2)
C_{p2}, mg·kg^{-1}	y = 0.252·x + 1.627	y = 0.223·x + 3.939

SUMMARY: Langmuir-type isotherm soil assays were conducted to estimate the mass distribution coefficient (k_{d2}), the soil adsorbed inorganic P pool (C_{p2}), and the soluble P pool in the soil interstitial water (C_{d2}) over a range of soil P concentrations for use in initializing soil P compartments in SWWRP-NSM. k_{d2} was not constant; but rather, varied in a negative logarithmic pattern as a function of increasing crop-available P concentration. This pattern may be attributable to declining soil buffering capacity for P as DPS increases and availability of unoccupied adsorption sites decreases. C_{p2} increased in a linear pattern, while C_{d2} exhibited a biphasic linear increase, in conjunction with increasing crop-available P. The latter pattern may also be related to the DPS.

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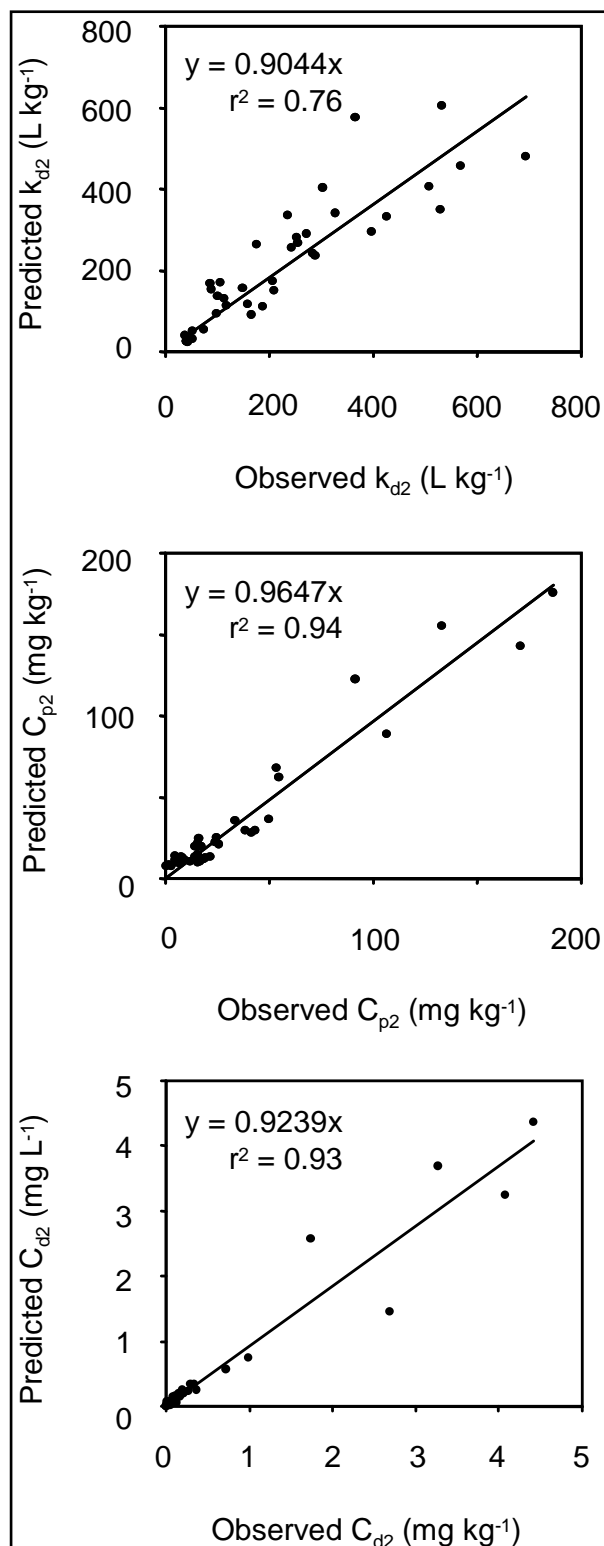
Figure 10. Predicted versus observed soil mass distribution coefficient (k_{d2}), initial adsorbed soil phosphorus (C_{p2}), and equilibrium phosphorus concentration (C_{d2}).

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